

The metallic state in disordered quasi-one-dimensional conductors

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The unusual metallic state in conjugated polymers and single-walled carbon nanotubes is studied by dielectric spectroscopy (8–600 GHz). We have found an intriguing correlation between scattering time and plasma frequency. This relation excludes percolation models of the metallic state. Instead, the carrier dynamics can be understood in terms of the low density of delocalized states around the Fermi level, which arises from the competition between disorder-induced localization and interchain-interactions-induced delocalization.

The finite conductivity of a metal at zero Kelvin is a consequence of the lattice-periodicity and the finite density of states at the Fermi level (E_F). By breaking translational symmetry, disorder localizes charge-carriers. Upon growing disorder, eventually a metal-insulator transition (MIT) occurs [1], the effect being the stronger the lower the dimensionality. In one dimension (1D) any disorder localizes the electronic states. The MIT in quasi-1D conducting polymers and single-walled carbon nanotubes is also disorder-driven, but its exact nature is under severe debate. Many authors claim the presence of a “heterogeneous” state in which the relevant disorder length-scale is large compared to the electronic correlation-length. In this case, the MIT corresponds to a percolation transition of metallic islands embedded in an amorphous matrix. [2–4] Other studies suggest that the MIT is of the Anderson type [1] with disorder occurring on length-scales equal or less than the electronic correlation-length. [5,6] Then, extended and localized states are separated in energy by the mobility edge (E_c), and the MIT occurs when E_F crosses E_c .

We have studied charge transport in polyaniline, polypyrrole, and single-walled carbon nanotubes. Preparation details are given elsewhere. [5,7,8] The temperature-dependent dc conductivity is shown in Fig. 1. Both single-walled carbon nanotubes and polypyrrole have a finite dc conductivity down to the lowest temperatures, indicating a metallic state. The dc conductivity of polyaniline vanishes when cooling, characteristic of an insulating phase. Clearly, all samples are on the boundary of the MIT. Unfortunately, these data alone are not sufficient to discriminate between the above mentioned models.

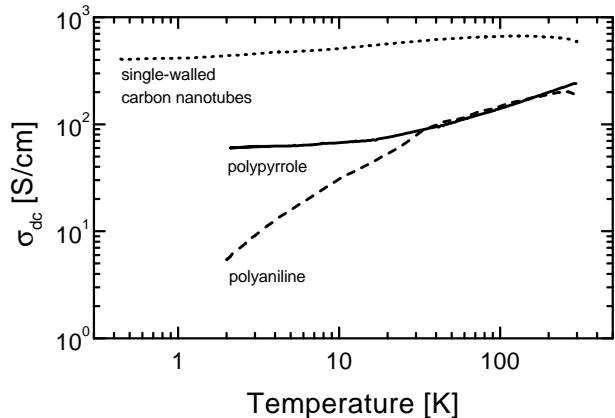


FIG. 1. Temperature dependent dc conductivity of three disordered quasi-1D systems. All samples are close to the MIT. Below 10 K the dc conductivities of polypyrrole and single-walled carbon nanotubes are almost temperature-independent implying a non-zero conductivity at zero Kelvin as expected for a metal. The dc conductivity of polyaniline vanishes when cooling, indicating that this sample is on the insulating side of the MIT.

Optical experiments have been widely used to study disordered quasi-1D conductors. [2,6–10] For conventional metals, the frequency ($\omega = 2\pi f$) dependence of the complex conductivity, $\sigma^* = \sigma + i\omega\varepsilon_0\varepsilon$ (ε_0 vacuum permittivity), is well explained in terms of the Drude free-electron model:

$$\sigma^*(\omega) = \frac{\varepsilon_0\omega_p^2\tau}{1 + i\omega\tau} \quad (1)$$

with τ the scattering time and

$$\omega_p = \sqrt{n e^2 / (\epsilon_0 m^*)} \quad (2)$$

the unscreened plasma frequency; n free-carrier density, e electronic charge, and m^* effective mass. For $\omega\tau < 1$, the dielectric constant (ϵ) is negative and the conductivity (σ) frequency-independent. For $\omega\tau > 1$, σ drops to zero, while ϵ increases and eventually becomes positive above ω_p . For normal metals $\omega_p \sim 1\text{--}10$ eV, and $\tau \sim 10^{-14}$ s. [11] Free-carrier absorption ($\epsilon < 0$ in the microwave and far-infrared regime) has been observed in polypyrrole [2], polyaniline [2,7], and single-walled carbon nanotubes. [8] Here $\sigma^*(\omega)$ is examined in the range 8–600 GHz (0.27–20 cm⁻¹, 0.033–2.5 meV) by means of complex-dielectric spectroscopy [8,7,12]. This technique covers both the microwave and far-infrared regime, and does not rely on Kramers-Kronig analyses.

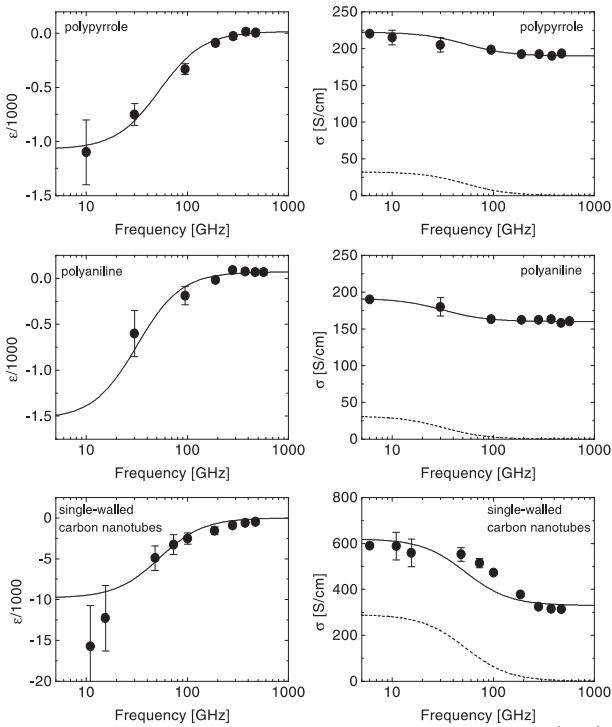


FIG. 2. Room temperature dielectric function (left) and conductivity (right) as a function of frequency for polypyrrole, polyaniline, and single-walled carbon nanotubes respectively. In view of the logarithmic scale, the value of σ_{dc} is plotted at $f = 6$ GHz. The drawn lines are fits to the data using the Drude equation with an extra (frequency independent) background conductivity and dielectric constant. The dielectric data are dominated by the free-carrier response. However, the free-carrier contribution to the conductivity (dashed lines) is less than 50%.

For all samples, at low frequency $\epsilon \ll 0$ as expected for a metal, see Fig. 2. However, contrary to Eq. (1), σ does not drop to zero but reaches a “plateau” at high frequency, indicating an additional absorption mechanism. By incorporating a frequency-independent background conductivity σ_b and dielectric constant ϵ_b in Eq. (1) the data can be excellently reproduced, see the solid lines in

Fig. 2. From the fits we find for respectively polypyrrole, polyaniline, and single-walled carbon nanotubes: ω_p (meV) = 7.3 ± 0.5 , 6 ± 1 and 22 ± 7 ; τ (ps) = 3 ± 0.5 , 5 ± 1 and 3 ± 1.5 ; ϵ_b = 18 ± 1 , 70 ± 10 and 0 ± 500 ; σ_b (S/cm) = 190 ± 10 , 160 ± 10 and 370 ± 50 . The free-carrier response of polyaniline shows that, for a sample just on the insulating side of the MIT, extended states become thermally occupied at finite temperature [13].

Fig. 3 displays the room temperature Drude parameters of disordered quasi-1D conductors, conventional metals [11], crystalline 1D conductors [14,15], graphite [16], and doped semiconductors. [17–19] The conducting polymers are given in black (dots this work, triangles Ref. 2), and reveal a remarkable empirical correlation $\tau \propto \omega_p^{-1.3}$. Comparable trends are observed for the doped-semiconductors. The open symbols correspond to the “second” plasma frequency observed in conducting polymers [2,6], and single-walled carbon nanotubes [9]. The conducting polymers and single-walled carbon nanotubes are very unlike conventional metals and crystalline 1D conductors. The scattering times are surprisingly long, and counter-intuitively even increase for the more disordered and “less metallic” samples.

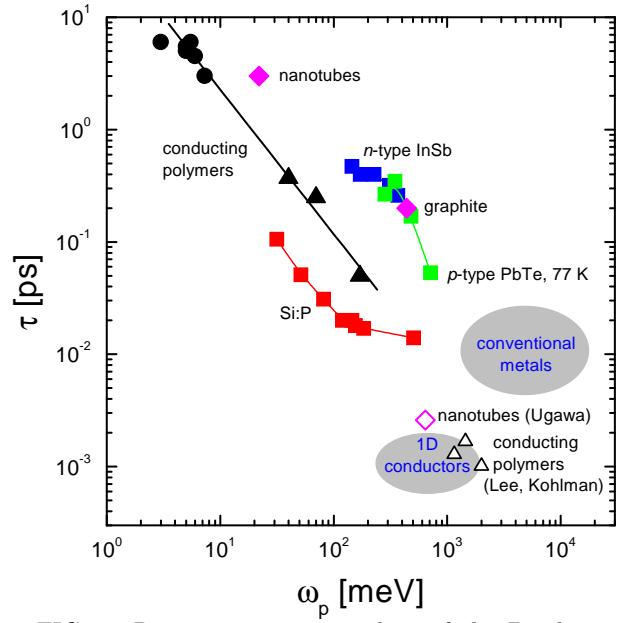


FIG. 3. Room temperature values of the Drude parameters τ and ω_p describing the metallic state in doped conjugated polymers and single-walled carbon nanotubes. For comparison the typical values of conventional metals, crystalline 1D conductors, graphite, and several doped semiconductors are indicated. In our view, the closed symbols correspond to the free-carrier response of 3D extended states, while the open symbols can be attributed to on-chain (1D) motion of charge-carriers. The empirical correlation $\tau \propto \omega_p^{-1.3}$ for the conducting polymers, seems to extrapolate to parameter ranges of conventional conductors.

The unusual carrier dynamics in conducting polymers

have been argued to indicate a quasi-1D percolating metallic state. [2] In this model, the long τ is explained in terms of one-dimensionality and the low ω_p as stemming from the small density of crystalline metallic regions. It was argued that, upon decreasing disorder, the fraction of metallic regions increases and this should increase ω_p [2]. However, the intrinsic conductive properties of metallic islands are not expected to depend on the concentration of such islands. For instance, in a bulk metal ϵ is zero at the plasma frequency. Based on effective medium calculations, Stroud [20,21] showed that the zero in ϵ at $\omega = \omega_p$ persists in a metal-insulator-composite for metal fractions above the percolation threshold, hence the plasma frequencies in the bulk and composite are the same. This is a natural consequence of the fact that ω_p only depends on the carrier density inside the percolating metallic path, and not on the free-carrier density in the total volume of the composite material. Indeed, recent experiments on thin quench-condensed Pb films demonstrated that ω_p in heterogeneous Pb films is independent of the fraction of Pb and almost equal to the plasma frequency of bulk lead [22]. In contrast, the plasma frequency in conducting polymers shows an increase of almost two orders of magnitude, see Fig. 3, at variance with the behavior of a percolating metallic network. Also, in terms of the heterogeneous model, Fig. 3 would imply that an increase of the fraction of metallic islands enhances the carrier scattering, which seems unlikely. Based on the above theoretical and experimental findings, we conclude that the unusual carrier-dynamics in quasi-1D conductors can not be explained in terms of a percolating fraction of highly conducting regions, but rather reflects the intrinsic transport properties of the weakly metallic state in these materials.

The similarity between conducting polymers and doped semiconductors, Fig. 3, provides a strong clue that the free-carrier dynamics in these materials is governed by a common mechanism. In doped semiconductors all carriers are delocalized, $n = n_{\text{doped}} \sim 10^{23}\text{--}10^{25} \text{ m}^{-3}$ [17–19]. In this three-dimensional, marginally metallic state the low ω_p 's arise from the low band-filling. In conducting polymers $n_{\text{doped}} \sim 10^{27} \text{ m}^{-3}$, the high band-filling should give $\omega_p \sim 1 \text{ eV}$, but the observed plasma frequencies are orders of magnitude lower. Apparently, only a fraction of the carriers are delocalized ($n \ll n_{\text{doped}}$).

The low dimensionality of these systems enhances disorder-induced localization. To obtain three dimensional (3D) extended states, inter-chain charge transfer is a prerequisite. The amount of 3D extended states will be governed by the competition between inter-chain overlap t_\perp and the strength of the disorder potential D . This is schematically depicted in Fig. 4, less disorder corresponds to increasing t_\perp/D and this increases the amount of delocalized states in the band. In this model, localized and delocalized carriers are not spatially separated, but are separated in energy by the mobility edge. As shown in Fig. 4, even if n_{doped} remains constant, both n and ω_p

will increase when t_\perp/D increases. In order to achieve a metallic state, the doping level must be high enough to have E_F in the region of delocalized states, which explains why the metallic state only occurs in highly doped polymers. Thus, the low ω_p 's in disordered quasi-1D conductors reflect that, due to small inter-chain overlap and strong disorder, the density of delocalized states is low, $n \ll n_{\text{doped}}$.

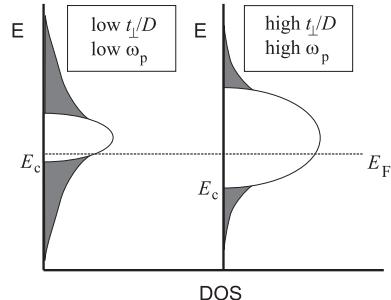


FIG. 4. Schematic drawing of the density of states (DOS) in disordered quasi-1D conductors as a function of t_\perp (inter-chain overlap) and D (disorder bandwidth). Localized states (white) are separated in energy by the mobility edge E_c from the extended states (gray). At constant doping level, when increasing the ratio t_\perp/D more extended states are formed, which gives a larger free-carrier density n and consequently a larger ω_p . The metallic state only occurs when $E_c < E_F$ which requires a high doping level together with large enough ratio t_\perp/D .

To quantify the above discussion, we use Eq. (2) and take as a typical density of states $g \sim 1 \text{ state}/(\text{eV ring})$ [2] and $\omega_p \sim 30 \text{ meV}$. As an estimate of n we consider a weakly metallic sample for which $E_F - E_c < k_B T$, so $n \approx k_B T g$, giving $n \sim 10^{25} \text{ m}^{-3}$ and $m^* \sim 15m_e$ (m_e electronic mass). Alternatively, when using a free-electron approximation, we find $n \sim 10^{24} - 10^{25} \text{ m}^{-3}$ and $m^* \sim 10m_e$. As expected, $n \ll n_{\text{doped}}$. The high m^* agrees with a low interchain overlap, which gives narrow electronic bands and hence heavy masses. From the derived m^* and n we estimate $E_F - E_c$ to be only a few meV. Indeed, $k_B T \gg E_F - E_c$, and the delocalized carriers behave classically. From the average velocity $\bar{v} = \sqrt{8k_B T/\pi m^*} \approx 3 \times 10^4 \text{ m/s}$, and $\tau \sim 5 \text{ ps}$ for $\omega_p \sim 30 \text{ meV}$, we find a mean free path $\ell \sim 10 \text{ nm}$. Since the electronic de Broglie wavelength is comparable or less than the mean free path, the Drude analysis seems justified.

In both single-walled carbon nanotubes and conducting polymers a second plasma frequency has been reported around 1 eV, with $\tau \sim 10^{-15} \text{ s}$. [2,6,9] These values match the on-chain parameters in crystalline 1D-conductors, and could reflect the motion of carriers which are not 3D-delocalized but confined to 1D chains. Lee *et al.* calculated that these carriers contribute 50–70% to the total dc conductivity [6], in agreement with σ_b in the fits of the GHz response (Fig. 2).

The empirical interrelation between τ and ω_p seems

generic for marginally metallic systems with low free-carrier density. The decrease of τ upon doping semiconductors has been suggested to result from impurity scattering. [19] However, for conducting polymers impurity or grain boundary scattering is not dominant at room temperature, since this would lower τ in the more disordered systems (lower ω_p). In a non-degenerate electron gas, due to screening, the electron-electron (e-e) scattering cross section $\Sigma \propto n^{-1}$, and $\tau_{e-e} \propto 1/(\bar{v}n\Sigma)$ is independent of n . Apparently, at room temperature electron-phonon (e-ph) scattering dominates. Since the e-ph scattering rate is proportional to the density of states, an increase of ω_p , reflecting the growing density of delocalized states, naturally leads to shorter τ 's. Indeed, the empirical correlation extrapolates to parameter ranges of conventional metals at room temperature, where e-ph scattering is known to govern the carrier dynamics.

Finally, we address the role of heterogeneity of the structure of disordered quasi-1D conductors, which lies at the heart of the controversy between "homogeneous" and "heterogeneous" disorder models. It is well established that the metallic state in conducting polymers requires careful preparation in order to minimize structural disorder. Diffraction experiments show that in the best metallic polymers the crystalline coherence length ξ is at most several nanometers [2,3,23]. Metallic islands could be formed when the crystalline coherence length is larger than the extent of electronic wavefunctions. However, from the present work we find that $\xi < \ell$, and this implies that the delocalized charge-carriers experience an average of the structural disorder. This corroborates our arguments that the carrier dynamics in quasi-1D conductors is not in agreement with percolation of metallic islands. In the model proposed here the role of structural (dis)order can be naturally explained. An increasing crystalline coherence length reflects that the polymer chains are mutually better ordered. This will favor interchain interactions and, at the same time, reduce the amount of disorder experienced by the charge carriers. Both effects enhance the metallic state.

The unusual carrier dynamics in conjugated polymers and single-walled carbon nanotubes has been consistently explained in terms of a three-dimensional marginally metallic state. The empirical correlation between τ and ω_p , which is observed in conventional, doped semiconductors and disordered quasi-1D conductors, is a consequence of the phonon-scattering mechanism and low density of extended states around E_F in these materials. In quasi-1D conductors the low free-carrier density can not be explained in terms of heterogeneity, but is governed by the competition between inter-chain charge transfer and disorder-induced localization onto 1D chains. Extrapolating the empirical correlation suggests the possibility of further improvement of the conductive properties of these

materials, though beyond those of conventional metals seems doubtful.

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